Electronic Supplementary Information

A Reproducible Gold SERS Substrate Assisted by Silver nanoparticles without Using Extra Aggregation Agents

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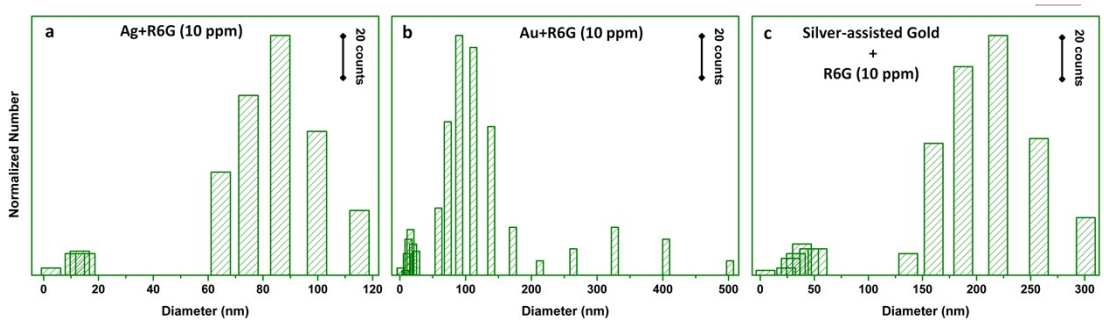

Figure S1. Sizes distribution of (a)Ag colloids+10 ppm R6G, (b)Au colloids+10 ppm R6G, (c)Silver-assisted Gold SERS substrate+10 ppm R6G.

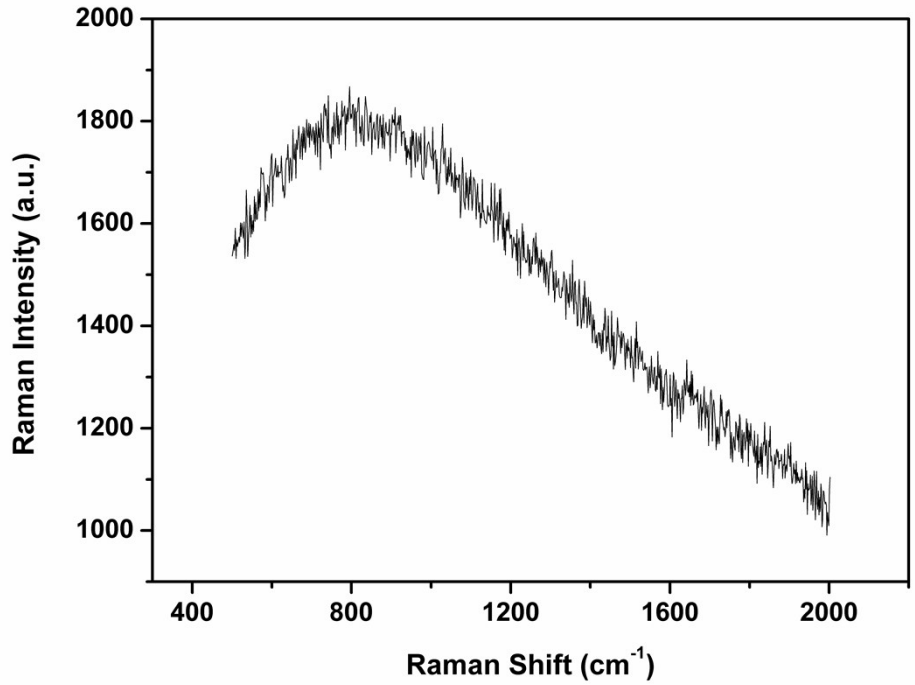

Figure S2. SERS measurement of 10 ppm R6G collected by Ag colloids. Raman spectra were recorded using a Renishaw inVia Raman Spectrometer. The laser power is 25 mW×0.0001%. The integration time was 10 s. The spot size of focus laser beam is 1 μm in diameter. The excitation wavelength is 532 mn.

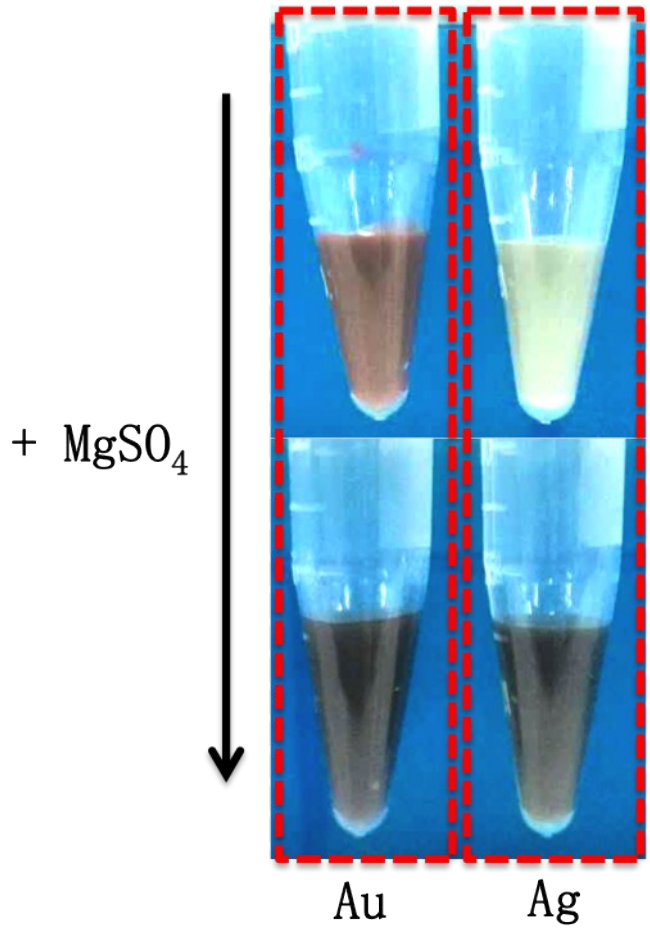

Figure S3. Color change of Au and Ag colloids before and after the addition of 0.25 M $MgSO_4$.

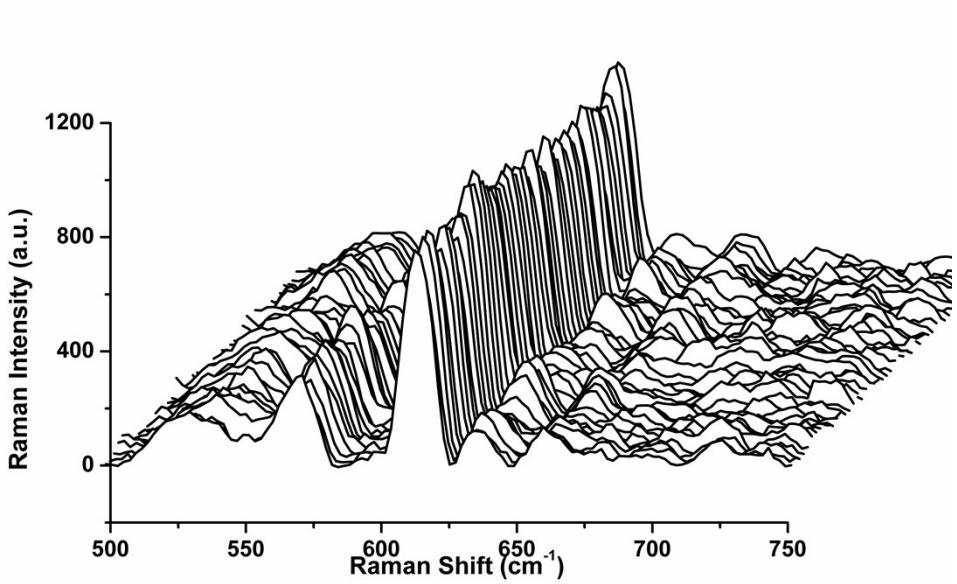

Figure S4. SERS spectra of 10 groups of samples (0.001 ppm R6G solution) collected by Silver-assisted Gold SERS substrate.

Table 1. Time fluctuation (RSD and SD of individual group of sample) and Sample to sample deviation (Total RSD and SD of 10 group of samples) of R6G SERS intensity at 612 cm^{-1} given in Figure S4.

Sample No.	1	2	3	4	5	6
% RSD	6.7	9.8	2.9	6.6	5.1	2.8
SD	46	64	19	44	35	20

Sample No.	9	10	11	12	Total RSD & SD
% RSD	3.0	6.1	7.0	5.3	16.3
SD	22	48	48	39	55

Estimation of the ratio expressed in number of particles

Because $HAuCl_4$ and $AgNO_3$ is reduced completely, the ratio expressed in number of particles can be estimated approximately by the following equation.

$$N_{\text{Ag NP}} = \frac{V_{\text{Ag colloids}} \times C_{\text{Ag-atom}} \times N_A}{\frac{4}{3}\pi r^3_{\text{Ag NP}} / \frac{4}{3}\pi r^3_{\text{Ag-atom}}} \quad (1)$$

$$N_{\text{Au NP}} = \frac{V_{\text{Au colloids}} \times C_{\text{Au-atom}} \times N_A}{\frac{4}{3}\pi r^3_{\text{Au NP}} / \frac{4}{3}\pi r^3_{\text{Au-atom}}} \quad (2)$$

where $V_{\text{Ag colloids}}$=10 mL, $V_{\text{Au colloids}}$=90 mL, $C_{\text{Ag-atom}}$=(2.5 mL×0.1 M)/250 mL=1 mM, $C_{\text{Au-atom}}$=0.294 mM, *r*3 AuNP=114 nm, *r*3 AuNP=85 nm, *r*3 Au-atom= *r*3 Ag-atom=1.44 Å. The ratio expressed in number of particles (Au to Ag) calculated is 6.3.